Defense Threat Reduction Agency
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DTRA-TR-14-45

TECHNICAL REPORT

Energetic Materials for WMD Defeat

Approved for public release; distribution is unlimited.

July 2014

HDTRA1-10-1-0116

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14. ABSTRACT

Two nitroiminotetrazole compounds, 1,2-bis(4,5-dihydo-5-nitroimino-1H-tetrazol-1-yl)ethane and bis(hydrazinium) ethylene bis(5-nitroiminotetrazolate) appeared to have properties that suggested further study to determine their value as replacements for RDX. They were synthesized in our laboratory (~2.5 - 3.0 grams) and shipped as aqueous solutions to NSWC, Indian Head for safety tests (impact sensitivity, friction sensitivity, and ESD). Results indicate that the two candidates, while superior to RDX in enthalpy of formation and detonation properties, with respect to the safety tests, they exhibit roughly RDX sensitivities. Thus, it is unlikely that they would be competitive as replacements for RDX.

15. SUBJECT TERMS
energetic materials, explosives, impact, friction, electrostatic discharge, tetrazoles, detonation properties

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CONVERSION TABLE

Conversion Factors for U.S. Customary to metric (SI) units of measurement.

MULTIPLY ⟶ BY ⟶ TO GET

TO GET ⟵ BY ⟵ DIVIDE

angstrom	1.000 000 x E -10	meters (m)
atmosphere (normal)	1.013 25 x E +2	kilo pascal (kPa)
bar	1.000 000 x E +2	kilo pascal (kPa)
barn	1.000 000 x E -28	meter^2 (m^2)
British thermal unit (thermochemical)	1.054 350 x E +3	joule (J)
calorie (thermochemical)	4.184 000	joule (J)
cal (thermochemical/cm^2)	4.184 000 x E -2	mega joule/m^2 (MJ/m^2)
curie	3.700 000 x E +1	*giga bacquerel (GBq)
degree (angle)	1.745 329 x E -2	radian (rad)
degree Fahrenheit	$t_k = (t^{o}f + 459.67)/1.8$	degree kelvin (K)
electron volt	1.602 19 x E -19	joule (J)
erg	1.000 000 x E -7	joule (J)
erg/second	1.000 000 x E -7	watt (W)
foot	3.048 000 x E -1	meter (m)
foot-pound-force	1.355 818	joule (J)
gallon (U.S. liquid)	3.785 412 x E -3	meter^3 (m^3)
inch	2.540 000 x E -2	meter (m)
jerk	1.000 000 x E +9	joule (J)
joule/kilogram (J/kg) radiation dose absorbed	1.000 000	Gray (Gy)
kilotons	4.183	terajoules
kip (1000 lbf)	4.448 222 x E +3	newton (N)
kip/inch^2 (ksi)	6.894 757 x E +3	kilo pascal (kPa)
ktap	1.000 000 x E +2	newton-second/m^2 (N-s/m^2)
micron	1.000 000 x E -6	meter (m)
mil	2.540 000 x E -5	meter (m)
mile (international)	1.609 344 x E +3	meter (m)
ounce	2.834 952 x E -2	kilogram (kg)
pound-force (lbs avoirdupois)	4.448 222	newton (N)
pound-force inch	1.129 848 x E -1	newton-meter (N-m)
pound-force/inch	1.751 268 x E +2	newton/meter (N/m)
pound-force/foot^2	4.788 026 x E -2	kilo pascal (kPa)
pound-force/inch^2 (psi)	6.894 757	kilo pascal (kPa)
pound-mass (lbm avoirdupois)	4.535 924 x E -1	kilogram (kg)
pound-mass-foot^2 (moment of inertia)	4.214 011 x E -2	kilogram-meter^2 (kg-m^2)
pound-mass/foot^3	1.601 846 x E +1	kilogram-meter^3 (kg/m^3)
rad (radiation dose absorbed)	1.000 000 x E -2	**Gray (Gy)
roentgen	2.579 760 x E -4	coulomb/kilogram (C/kg)
shake	1.000 000 x E -8	second (s)
slug	1.459 390 x E +1	kilogram (kg)
torr (mm Hg, 0^0 C)	1.333 22 x E -1	kilo pascal (kPa)

*The bacquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.

**The Gray (GY) is the SI unit of absorbed radiation.

Executive Summary – HDTRA1-10-1-0116

I. Research objectives

Scale up synthesis of two nitroiminotetrazole compounds - 1,2-bis(4,5-dihydro-5-nitroimino-1H-tetrazol-1-yl)ethane and bis(hydrazinium) ethylene bis(5-nitroiminotetrazolate) – for further characterization. Complete the safety testing (friction, impact, and ESD) measurements on the two compounds.

II. Summary of topics addressed

Scale up synthesis of two salts

A. 1,2-bis(4,5-dihydro-5-nitroimino-1H-tetrazol-1-yl)ethane
B. bis(hydrazinium) ethylene bis(5-nitroiminotetrazolate)

Safety testing of two salts

A. friction, impact, and ESD testing

III. Work accomplished

The goal of this work was to determine the suitability of two compounds that were first synthesized under HDTRA1-07-1-0024 (vide supra) to be transitioned to 6.2 as possible replacements for RDX. These materials had been shown in our previous work to have detonation properties, thermal stabilities, densities, enthalpies of formation and impact sensitivities that were very competitive with RDX. The compounds were synthesized in 2.5-3.0 g amounts and shipped as aqueous solutions to Indian Head for testing. The safety testing measurements handled via a subaward with Dr. Joseph D. Mannion, Research & Technology Department, Building 600 Naval Surface Warfare Center, Indian Head Division (NSWC IHD), Indian Head, MD 20640-5102. NSWC IHD performed three small-scale safety testing measurements: ERL Bruceton Impact (2.5 kg, type 12 tools), BAM Friction, and ABL Electrostatic Discharge, with the data referenced to the RDX 'A' standard. Each set of tests required ~3 grams of material.

IV. Personnel supported

Ms. Thao Vo – Graduate student – US citizen

Report

III. Work Accomplished

Over the last decade, the syntheses of energetic hetrocyclic compounds have attracted considerable interest. Environmental contamination by nitro compounds is associated principally with the explosives industry and military testing of explosives. Compounds with a high nitrogen-atom content are potential candidates for replacing common explosives like 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), 2,4,6,8,10,12-(hexanitrohexaaza)cyclododecane (CL-20), 1,3,3-trinitroazetidine (TNAZ), 1,1-diamino-2,2-dinitroethene (FOX-7), (having high densities and energies utilizing substantial cage strain) and trinitrotoluene (TNT) or for use in propellants when combined with a suitable oxidizer. The combination of a tetrazole ring with energetic groups containing oxygen such as nitro groups, nitrate esters, or nitramines is of particular interest. In order to meet the continuing need for improved energetic materials, the synthesis of energetic heterocyclic compounds has attracted considerable interest due to their rather large densities, and high heats of formation.

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials and considerable attention is focused on azoles as energetic compounds especially the tetrazole series. Energetic materials based on tetrazoles show the desirable properties of high N-atom contents as well as thermal stabilities due to aromaticity. Tetrazole compounds containing nitro imino groups as energetic materials have been intensively investigated both theoretically and experimentally because the nitro imino group can offer improved density, oxygen balance and high heat of formation. Additionally the decomposition of these compounds results in the generation of nitrogen gas which makes them very promising candidates for applications requiring environmentally friendly energetic materials. The high energetic density materials (HEDM) with the highest performance (RDX, HMX) belong to the class of typical organic ring and cage molecules.

Nitroiminotetrazoles are of special interest because they combine both the oxidizer and energetic nitrogen-rich backbone in one molecule. The simple system of 5-(nitroimino)tetrazoles was prepared by treatment of nitroaminoguanidine with KNO_2 and concentrated HCl nearly 60 years ago. In 1957, 1-alkyl substituted 5-nitroiminotetrazole was extensively investigated by two different methods: 1) the direct nitration of 1-methyl-5-aminotetrazole with nitric acid; and 2) the reaction of potassium methylnitramine and cyanogen bromide to form methylnitrocyanamide. After interaction of methylnitrocyanamide and hydrazoic acid, 1-methyl-5-nitroiminotetrazole was isolated. More recently complete characterization of nitroiminotetrazole and its salts were reported as HEDM. The heats of formation were determined for each nitroiminotetrazole by bomb calorimetric measurements, and the density in the crystalline state were determined by single-crystal X-ray diffraction.

The continuing need for improved energetic materials to combat WMD has catalyzed a wide range of attempts to synthesize new energetic heterocyclic compounds; in particular those with rather high densities, positive heats of formation, and competitive detonation properties. Under our previous grant (HDTRA 1-07-1-0024 – expired 12/19/2009), we have synthesized a very large number of energetic materials which fall

into the high-energy high nitrogen compound category. Among these there are two nitroiminotetrazole compounds, 1,2-bis(4,5-dihydro-5-nitroimino-1H-tetrazol-1-yl)ethane and bis(hydrazinium) ethylene bis(5-nitroiminotetrazolate),[1,2] that appeared to have properties that warranted further study to determine their value as competitors with or replacements for currently used energetics, e. g. TNT, RDX, HMX (Table 1). Included in the Table is the data (impact sensitivity, friction sensitivity, and ESD), that was obtained from Dr. Mannion at IHD combined with Idaho data which prompted the interest in examining these two compounds further. The complete IHD data is included in APPENDIX 1.

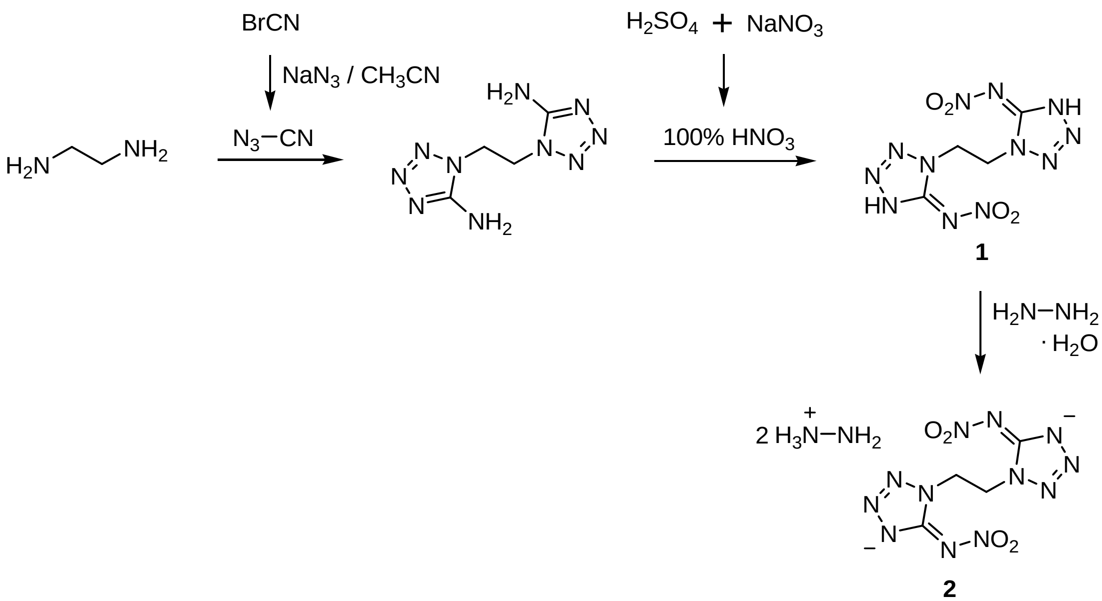
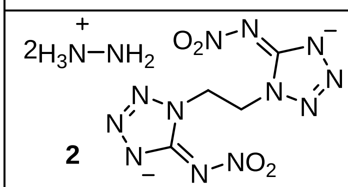
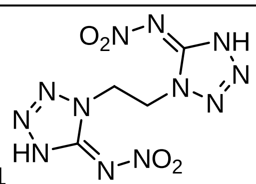


Table l. Selected properties of two new energetic compounds compared with RDX.

Compounds	m.p.[a] °C	Density g cm^{-3}	$\Delta_f H°_{298}$[a] kJ g^{-1}	P^b GPa	vD^c m s^{-1}	IS[d] J	IS*[e] 50% hgt. (cm)	F*[f] N	ESD*[g] J
 2	223	1.73	3.05	35.3	9478	10	13 (H)[h]	108 (M)	0.853 (M)
 1	194 dec.	1.86	3.63	38.2	9329	10	10 (H)	60 (M)	0.095 (M)
RDX, class 5	230 dec.	1.82	0.42	35.2	8977	7.4	16 (M)	108 (M)	0.037 (M)

[a] enthalpy of formation [Gaussian 03 (Revision D.01)]; [b] detonation pressure (Cheetah 5.0); [c] detonation velocity (Cheetah 5.0); [d] impact sensitivity (BAM fallhammer); ***** Data from Indian Head; [e] ERL impact 50% hgt. (cm); [f] BAM Friction 10 TIL (newtons); [g] ABL ESD 20 TIL - electrostatic discharge (Joules); [h] L = low sensitivity; M = medium sensitivity; H = high sensitivity.

Summary

Although the two candidate compounds, **1** and **2**, are roughly equivalent to RDX, (class 5) in properties such as melting point, and density, they have considerably greater heats of formation, and meet or exceed its detonation properties. With respect to impact sensitivity, friction sensitivity and ESD sensitivity, all are rated as medium sensitivity as is RDX with the exception of **2** that is rated as high sensitivity with respect to impact sensitivity. Therefore, it is unlikely that these two compounds will be useful for further study as competitive explosives. However, in other formulations they may be of value.

[1] Joo, Y.-H.; Shreeve, J. M. "Energetic Mono, Di-, and Trisubstituted Nitroiminotetrazoles," *Angew. Chem. Int. Ed.* **2009,** *48,* 564-567.
[2] Joo, Y.-H.; Shreeve, J. M. "Energetic Ethylene- and Propylene-Bridged Bis(nitroiminotetrazolate) Salts," *Chem. Eur. J.* **2009**, *15*, 3198-3203.

APPENDIX

5100
Ser R35DR/1084/dr
15 July 2011

MEMORANDUM

From: Daniel Remmers R35DR
To: Joe Mannion R11JM

Subj: SENSITIVITY TESTING FOR NITROIMINO TETRAZOLES

Ref: (a) Request by J. Mannion, Code R11JM, on 30 June 2011.

1. As requested by reference (a), the following information is forwarded:

Sample	ERL Impact 50% hgt. (cm)	BAM Friction 10 TIL (newtons)	ABL ESD 20 TIL (joules)
ethylene bis 5-nitro imino-tetrazole	10 (H)	60 (M)	0.095 (M)
dihydrazunium ethylene bis 5-nitro imino-tetrazole	13 (H)	108 (M)	0.853 (M)
RDX, class 5	16 (M)	108 (M)	0.037 (M)

L = low sensitivity M = medium sensitivity H = high sensitivity

2. The tests were completed on July 7, 2011 in accordance with SOPs P30981, P30979, and P30995. Testing was conducted at NSWC Indian Head, in the Hazard Characterization Lab, Building 888.

3. If there are any questions, please call the Hazard Characterization Group at 301-744-4109.

Daniel Remmers, Code R35DR

Phillip Vaughn

Phil Vaughn, Code R35

ERL BRUCETON IMPACT TEST

sample name: ethylene bis 5-nitro imino-tetrazole
sample ID:
sample prep: powder
requester: Joe Mannion, R11JM
operator: E. Peterson

date: 7/7/11
temperature: 23 °C
relative humidity: 46 %
surface: 180A garnet paper

	height (cm)	result	comments
pre-shots -->	25.5	1	pop/smoke
	20	1	pop/smoke
	12.5	0	no reaction
	16	1	pop/smoke

ERL Bruceton impact tester
with type 12 tools,
2.5 kg drop weight,
35 mg per drop,
building 888, room 105

shot #	hgt. (cm)	result	comments
1	12.5	0	
2	16.0	1	pop/smoke
3	12.5	0	
4	16.0	1	pop/smoke
5	12.5	1	pop/smoke
6	10.0	0	
7	12.5	1	pop/smoke
8	10.0	0	
9	12.5	1	pop/smoke
10	10.0	1	pop/smoke
11	8.0	0	
12	10.0	1	pop/smoke
13	8.0	1	pop/smoke
14	6.5	0	
15	8.0	0	
16	10.0	1	pop/smoke
17	8.0	1	pop/smoke
18	6.5	0	
19	8.0	1	pop/smoke
20	6.5	0	
21	8.0	0	
22	10.0	0	
23	12.5	0	
24	16.0	0	
25	20.0	1	pop/smoke

available levels (cm)	log heights
5.0	0.7
6.5	0.8
8.0	0.9
10.0	1.0
12.5	1.1
16.0	1.2
20.0	1.3
25.5	1.4
32.0	1.5
40.5	1.6
50.5	1.7
64.0	1.8
80.5	1.9
101.0	2.0
127.5	2.1
160.5	2.2
202.0	2.3
254.5	2.4
320.0	2.5

1 = positive (fire)
0 = negative (no-fire)

50% height	standard deviation
10 cm	**0.26** log units

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